

Detection of the explosive nitroaromatic compound simulants with chemosensory systems based on quartz crystal microbalance and chemiresistive sensor arrays

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Abstract. The work is devoted to investigations of possibility of rapid detection and subsequent identification of explosive substances by using the arrays of two types of sensor elements: quartz crystal microbalances and chemiresistive electrodes. Thin layers of calixarene compounds and composites of electrically conductive polymers, respectively, were used as the sensitive coatings. Several types of nitroaromatic compounds from nitrotoluene series were chosen as simulants of explosive substances: O-Nitrotoluene (2-MNT) and Nitrobenzene (MNB), the concentration of these volatile compounds varied from 10 to 100 ppm. The observed detection threshold, depending on the type of analyzed explosive simulants, was within the range of 1 to 10 ppm for quartz crystal sensors with calixarene sensitive films, and the response time was within 10...20 s for quartz crystal sensors and up to 1 min for chemiresistive sensors. It has been shown that among the tested calixarenes there are samples with high selective sensitivity. The possibility of qualitative identification of explosives at relatively low concentrations by using the statistical methods of chemical patterns recognition (the so-called “electronic nose”) has been demonstrated.

Keywords: quartz crystal resonator, calixarene receptor, chemiresistive electrode, sensor array, electroconductive polymer, explosive substance.

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1. Introduction

At present, the complex and expensive methods of mass spectrometry, different types of spectroscopy, chromatography are, for the most part, used to detect and identify explosive substances [1–4]. At the same time, much simpler and cheaper methods of both detection and identification of the specified substances have been developed using sensor arrays and statistical methods of chemical patterns recognition (the so-called “electronic nose” technology). In particular, relatively simple types of primary signal transducers are known, suitable to detect specific analytes in the relevant concentration range: 1) quartz crystal microbalance (QCM), the principle of operation of which consists in measuring the

oscillation frequency shift of the quartz resonators covered with thin layers of sensitive materials, due to changes in the mass of these layers upon adsorption of gas molecules, and 2) chemiresistive sensors that register changes in electrical resistance or conductivity of the electrodes covered with (nano)composite layers of electrically conductive polymers upon interaction with molecules of gaseous analytes.

Sensors of the first type are widely used to determine the thickness of deposited layers, monitoring of gaseous [5] and liquid media [6]. Layers of calixarene materials capable of forming supramolecular complexes with gas molecules and, accordingly, selectively detect the latter are often applied as sensitive coatings for these sensors. Having molecular cavities different in their

structure and size, calixarenes (CA) are suitable for creating effective receptor platforms with specific adsorption properties. CAs can be immobilized in the form of thin layers on the surfaces of quartz crystal resonators to create QCM sensor elements. Due to rather weak intermolecular interactions between the calixarene compounds and analyte molecules, these sensors are characterized by fast adsorption and desorption kinetics, which is an important property for chemical sensing. In particular, calix[4]arenes are promising for the design of highly efficient selective adsorbents of volatile organic substances [7, 8].

Several calixarenes functionalized with different types of organic groups have been used for investigations on QCM-based chemosensory system. Utilization of the new original modified calixarenes which possess different (in terms of the size and nature of the formed non-covalent bonds) internal molecular cavities, as effective receptors immobilized on the surface of quartz resonators, seems perspective in the creation of new sensor materials with specific properties, for example, fast adsorption kinetics due to the absence of internal diffusion and swelling of the material, which is an important factor for their sensitivity to gases. These nanomaterials and sensitive layers (or thin films) are the basis of sensor technologies and have significant potential both from the viewpoint of fundamental research and for practical implementation in sensor devices, which is especially important for environmental monitoring, protection against terrorist threats and ensuring people's safety [9].

Among the selected types of calixarenes, some of the compounds are thiacalixarenes. Larger thiacalix[4]arenes, which contain cation-accepting sulfur atoms as part of the macrocyclic structure, are used as platforms for designing the highly selective receptors. However, the literature describes only a few works in which thiacalix[4]arene derivatives found their practical application in sensory chemistry. The presence of sulfur atoms in the macrocyclic platform, as well as the possibility of functionalization of the upper and (or) lower rim, make thiacalix[4]arenes attractive in terms of obtaining highly effective and selective receptors [10, 11].

Sensors of the second type, based on chemiresistive electrodes, use nanocomposites of dielectric polymers with nanoparticles of carbon or noble metals [12], or electrically conductive polymers (ECP) [13–15] and their nanocomposites with dielectric polymers or inorganic and carbon nanoparticles [16, 17] to form the sensitive layers. Among these materials, ECP (polyaniline, polypyrrole, polythiophene, their derivatives) occupy an important place due to unique combination of chemical, electrical, photoelectric, electrochromic and sensory properties, a developed system of π -conjugated bonds, *etc.* The advantages of materials containing ECP are the relatively simple methods of synthesis and formation, chemical stability, synthetic versatility, and high sensitivity to volatile organic compounds at room temperature [13–15, 18–20]. Sensor elements based on ECP and their

nanocomposites reversibly react to gaseous analytes by changing their electrical conductivity (resistance) [18–20]. Such sensors exhibit low power consumption and compatibility with simple measuring equipment.

Based on our previous experience [21–23], several types of such ECP materials sensitive to volatile organic substances within the concentration range of 1...1000 ppm were selected. These are composite films of electrically conductive polymers having a “core-shell” type structure of the matrix polymer (core) clad in ECP (shell), combining a template polymer matrix with formation of an electrically conductive nanoshell of ECP on its surface.

Application of both specified types of sensor transducers with different mechanisms of sensor responses for characterization of the same gas mixtures should lead to an increase in reliability of the obtained results. Based on this, the purpose of this work was to investigate the possibility of rapid detection and subsequent identification of explosive volatile substances by using arrays of quartz crystal and chemiresistive sensors, with subsequent application of statistical analysis methods to the data obtained from sensor arrays.

2. Materials and methods

Eight types of calixarene compounds with different functional groups (a list of which is given in Table 1) and three types of chemoresistant nanocomposites, different in nature of the components and with the “core-shell” morphology of their nanoparticles, were selected for research:

1) the nanocomposite of submicron (~200 nm) polyvinylidene fluoride (PVDF) particles coated with a shell of poly(3-methylthiophene) (P3MT) doped with chloride anions (PVDF/P3MT-Cl);

2) the nanocomposite of ~20 nm titania nanoparticles coated with a shell of polyaniline (PANI) doped with dodecylbenzenesulfonic acid (DBSA) (TiO_2 /PANI-DBSA); and

3) the nanocomposite of multi-walled carbon nanotubes (CNT) with a shell of P3MT doped with chloride anions (CNT/P3MT-Cl).

Two types of nitroaromatic substances from the range of nitrotoluenes were selected as imitators of explosive substances (Table 2).

2.1. Quartz crystal microbalance technique

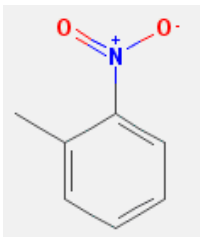
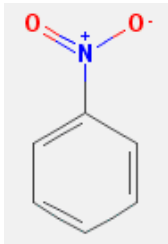
The QCM technique consists in measuring the frequency shift of quartz resonator due to adsorption or desorption of environmental molecules on the quartz surface. The dependence between the change in quartz resonator oscillation frequency Δf and the mass Δm adsorbed on its surface is described by Sauerbrey equation [25]:

$$\Delta f \approx -\frac{2f_0^2}{A\sqrt{\rho_q \mu_q}} \Delta m,$$

Table 1. List of selected types of calixarenes.

No	Name
1	Tetra(<i>tert</i> -butyl)-tetra(nitrilobutyloxy)-thiacalix[4]arene (CA911)
2	Tetraamino-25,27-dipropyloxy-26,28-didodecyloxy-calix[4]arene (CA1050)
3	Tetra(<i>tert</i> -butyl)-tetra(1'-piperidinecarbonylmethoxy)-thiacalix[4]arene (CA1078)
4	Tetra(<i>tert</i> -butyl)-tetra[N-(dicarboxymethyl)aminocarbonylmethoxy]-thiacalix[4]arene (CA1079)
5	Complex of tetraammonium-25,27-dihexyloxy-thiacalix[4]arene tetrachloride and diisopropylethylammonium salt of 3,6-dicarboxy-9-ethylcarbazole (CA1089)
6	Tetraammonium-25,27-dihexyloxy-thiacalix[4]arene tetrachloride (CA1090)
7	Tetraammonium-25,27-dipropyloxy-26,28-didodecyloxy-calix[4]arene tetrachloride (CA1091)
8	Tetraammonium-tetrahydroxy-thiacalix[4]arene tetrachloride (CA1092)

Table 2. Characteristics of selected imitators of explosive substances.

2-Nitrotoluene (2-MNT)	$C_6H_4(CH_3)(NO_2)$ 	Saturated vapor pressure: 0.15 mm Hg at 20 °C; 0.25 mm Hg at 25 °C	[24]
Nitrobenzene (MNB)	$C_6H_5NO_2$ 	Saturated vapor pressure: 0.24 mm Hg at 20 °C; 0.32 mm Hg at 25 °C	[24]

where f_0 is the quartz fundamental frequency, ρ_q is the quartz density, μ_q is the quartz elastic modulus, A is the surface area. For standard radiotechnical quartz resonator (AT-cut, 10 MHz fundamental frequency, 4 mm effective surface diameter) substituting values $\rho_q = 2.65 \text{ g/cm}^3$ and $\mu_q = 2.95 \cdot 10^{11} \text{ g/cm} \cdot \text{s}^2$ one can obtain $\Delta m \approx -k\Delta f$, where $k = 0.5 \text{ ng/Hz}$. That is, the sensitivity of the method is quite high, which makes its use common in various fields

of science and technology, in particular in sensor science [26]. The Sauerbrey relationship is valid up to 1% frequency shift relative to the fundamental frequency, the sensitive film should be thin and dense, tested medium should not be viscous.

To carry out the study of adsorption properties inherent to the synthesized samples, an 8-channel gas analytical sensory system of the non-flow type

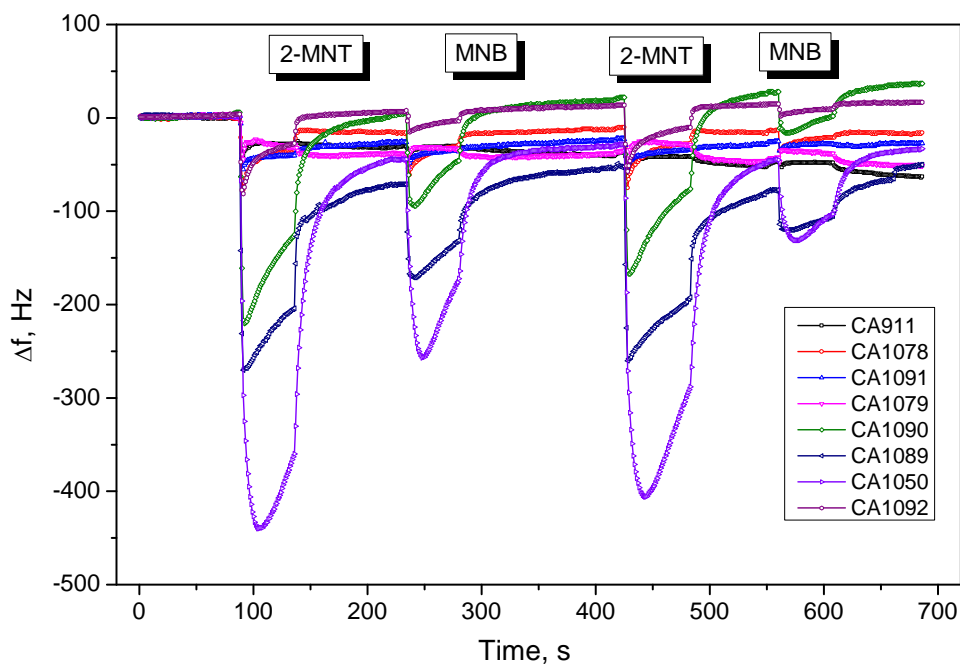


Fig. 1. Kinetics of sensor array responses on the analyte injection with the concentration close to saturated vapor. (Color online.)

(“electronic nose”) with the necessary set of equipment (gas cell, gas supply system, cleaning system), electronic part (resonance frequency measurement boards, PC interface, generators for excitation of quartz resonators) and software developed in the V. Lashkaryov Institute of Semiconductor Physics, NAS of Ukraine, has been used. Between successive injections of the analyte, the cell with sensor array was purified with clean dry air until the sensor frequency was restored to its initial value. A detailed description and principle of operation of the chemosensory system based on a quartz microbalance can be found in [8]. The experiments were carried out under normal conditions (20 °C, 760 mm Hg). Calixarene molecules with different functional groups, synthesized at the Institute of Organic Chemistry according to the method described in [27], were used as sensitive layers. Selected calixarenes, the list of which is given in Table 1, demonstrated good sensitivity and selectivity to various classes of volatile molecules in previous studies [28].

Immobilization of the calixarene sensitive layers was performed by means of spin-coating or drop-spreading from the 1 mg/ml solution of calixarene in chloroform. After evaporation of the solvent in the flux of dry air, a sufficiently uniform film was formed on the quartz surface. The thickness of the deposited film was estimated by the ellipsometric method and was 100...110 nm, which corresponded to a frequency shift of 5000 ± 500 Hz. For the eight-channel sensory system, sensor elements were chosen close in “effective thickness”, which makes it possible to more correctly compare compounds, because the magnitude of the response, as a rule, is directly proportional to the thickness of sensitive layer.

2.2. Chemiresistive electrodes

To prepare chemiresistive sensors, layers of selected nanocomposites with different ECPs were applied from their 0.5...2 wt.% dispersions in chlorobenzene onto the raster gold electrodes formed on glass-ceramic substrates. Gold electrodes with a thickness of about 150 nm were obtained using thermal evaporation in vacuum. Each sensor element contained 20 pairs of raster electrodes with a size of 1050×20 μm , separated by a gap of 20 μm . The resulting sensitive layers had an area of about 2 mm², with a typical layer thickness of 100 to 200 nm. Two chemiresistive elements of the same type were produced simultaneously on each substrate.

The sensor response was defined as the change in direct current through each chemiresistor upon the influence of changes in the surrounding environment, with an adjustable excitation voltage applied to the sensor. The physical value that was directly measured in the experiment was the voltage at the output of a transimpedance converter, directly proportional to the electrical conductivity of the sensor sensitive layer. Therefore, the response of sensor can be defined as a change in the value of the sensitive element conductivity (or its resistance), when it interacts with analyte vapors. A more detailed description of the measuring setup for an array of chemiresistive sensors is given in [34–36]. Due to the significant spread of the electrical parameters of the sensors, the values of the registered responses were converted into a relative change in the sensor resistance:

$$\delta R = \frac{R - R_0}{R_0} = \frac{U_0 - U}{U},$$

where R and U are, respectively, the resistance of the sensor and the voltage at the output of the secondary transducer after the exposure to an analyte; R_0 and U_0 are the initial values of the resistance and the output voltage in the absence of analyte vapors.

The exposure of individual analytes was performed using a gas injection system, each measurement was carried out for 2 min, and the chamber with the installed sensors was repeatedly blown-through with the room air between measurements. The desired concentration of the analyte was formed by successive dilutions of its saturated vapor (taken at 20 °C) with the room air, for this purpose a set of 50 ml plastic syringes was used. A separate syringe was used for each analyte.

3. Results and discussion

3.1. Studying the sensitivity of sensory elements with calixarene sensitive layers to explosive compound simulants

Kinetic dependences of the sensor responses on injection of analytes with a concentration level close to saturated vapor under “normal conditions” into the operation cell is shown in Fig. 1. Re-injection after 3 min showed a good reproducibility of the signals, while the slightly smaller amplitude upon re-injection is probably related to the

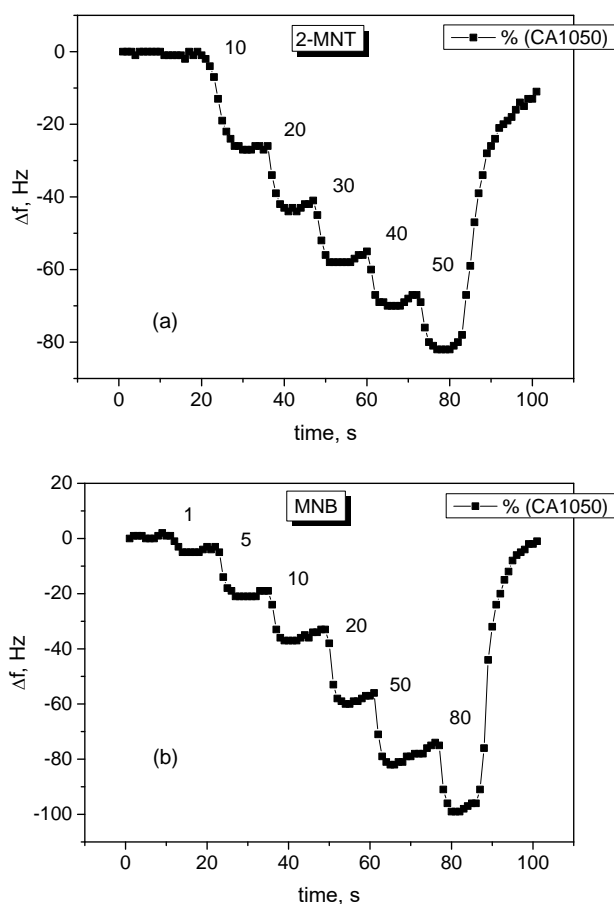


Fig. 2. Kinetics of the responses of the sensor with a sensitive CA1050 film to the consequent injection of 2-MNT (a) and MNB (b) into the operation cell.

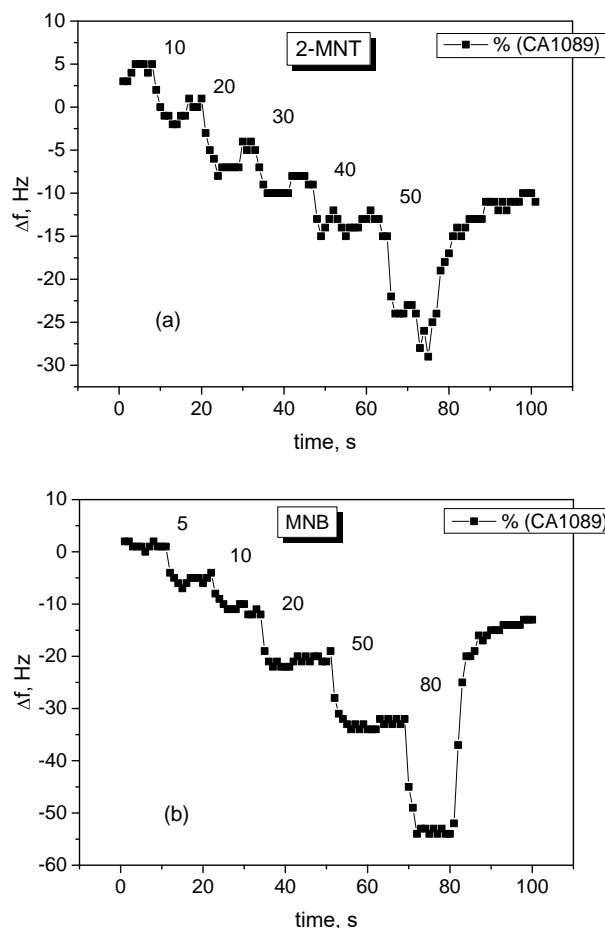


Fig. 3. Kinetics of the responses of the sensor with a sensitive CA1089 film to the consequent injection of 2-MNT (a) and MNB (b) into the operation cell.

incomplete recovery of the concentration in the sample preparation volume for the given time.

Sensors with the films of types CA1050, CA1089 and CA1090 turned out to be the most sensitive. They react almost instantly to the injection of analytes and recover well. Responses from these three sensors are almost instantaneous, while recovery processes differ significantly. The sensor with the CA1050 film recovers almost to the initial value, the recovery of the sensor with the CA1089 compound takes a long time or requires an increase in temperature. The processes that occur during the restoration of the sensor with CA1090 lead to an increase in the frequency relative to the original one.

Responses of these sensors on the injection of mono-nitrotoluene (2-MNT) and mono-nitrobenzene (MNB) vapors into the cell were investigated in detail in a single-channel sensory system in order to determine their sensitivity and detection threshold.

The kinetic dependences of the responses of sensors with sensitive films CA1050, CA1089 and CA1090 to the consequent injection of 2-MNT (a) and MNB (b) vapors into the operation chamber are presented in Figs 2, 3 and 4, respectively. Numerical symbols in the plots show the concentration of analyte in ppm.

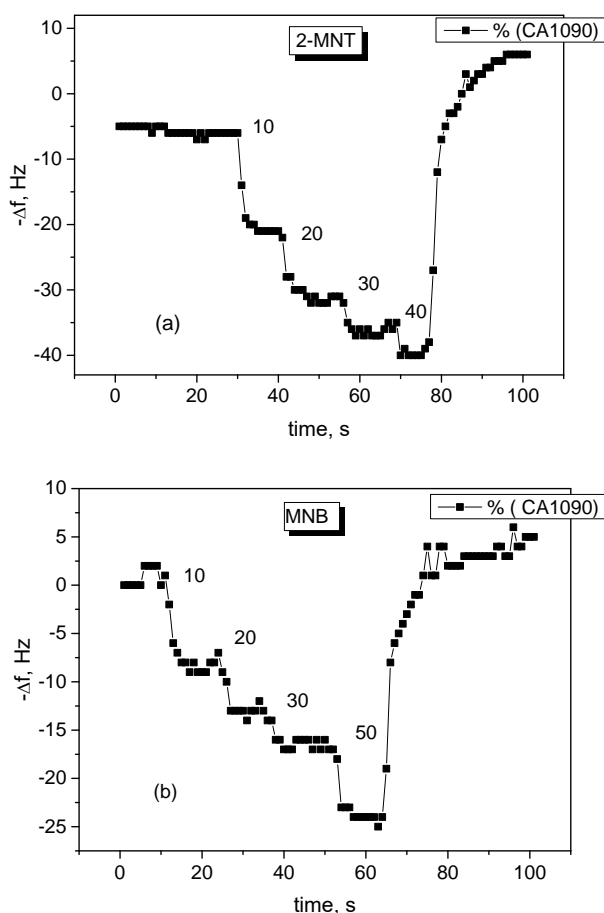


Fig. 4. Kinetics of the responses of the sensor with a sensitive CA1090 film to the consequent injection of 2-MNT (a) and MNB (b) into the operation cell.

As in the case of sensors interaction with high concentration of analytes, the responses to the consequent injection of 2-MNT and MNB starting from the limit of sensitivity, the sensors show fast, at the level of units of seconds, responses to the injections of analytes. The recovery processes have some differences. The processes of formation and decomposition of complexes in these quite complex systems require detailed research with the involvement of other analytical methods.

Fig. 5 shows the concentration dependences for the most sensitive types of QCM sensors in relation to the studied imitators of explosive substances 2-MNT and MNB in the range of low concentrations from 1 ppm. The sensitivity threshold for these types of sensors was within 1 ppm, when being measured using the QCM method.

For further analysis regarding identification of imitators of explosive substances, the responses of the sensor array from all 8 QCM sensors were projected onto the corresponding factor planes by using the statistical method of principal component analysis (PCA) [29]. The diagram of patterns recognition of chemical images of two types of simulators (2-MNT and MNB) with the concentrations close to those in the saturated vapors

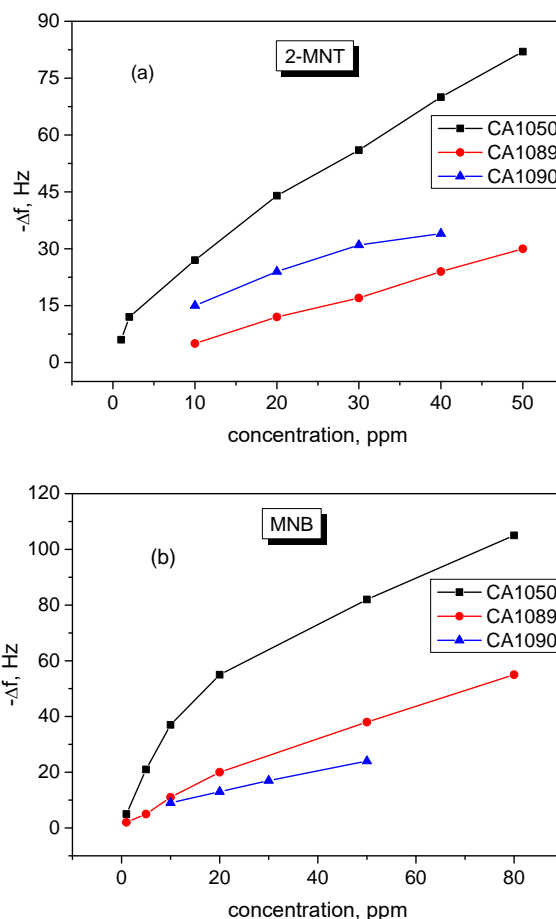


Fig. 5. Concentration dependences of the responses of the sensors with sensitive films CA1050, CA1089 and CA1090 towards 2-MNT (a) and MNB (b) explosive simulants.

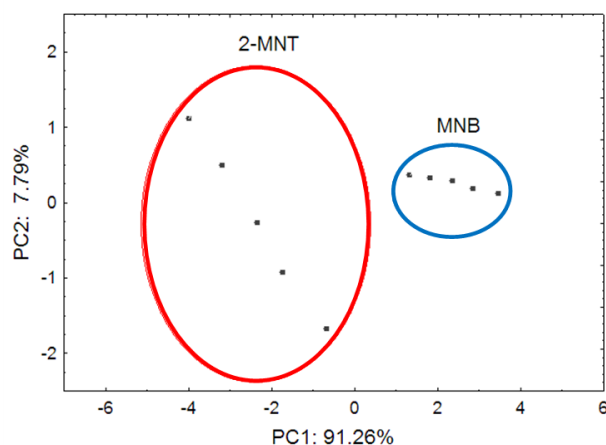


Fig. 6. The diagram of recognition of the chemical images of 2 types of explosive simulants (2-MNT and MNB) by using the PCA method; points in the outlined circles correspond to 5 repeated injections with the concentrations close to those in the saturated vapors.

is presented in Fig. 6. It can be seen that both substances are well identified with each other.

3.2. Investigation of the sensory characteristics of chemiresistive electrodes with respect to explosive simulants

As already mentioned, three types of chemiresistive films were selected for testing with the explosive substance simulants: CNT/P3MT-Cl, TiO₂/PANI-DBSA and PVDF/P3MT-Cl. The measurement method was similar to that described in [22, 23].

In the course of test measurements, it was found out that the sensors with TiO₂/PANI-DBSA and PVDF/P3MT-Cl sensitive films demonstrated appreciable responses only at the analyte concentrations above 200 ppm. For lower analyte concentrations (10...100 ppm) only the CNT/P3MT-Cl film was sufficiently sensitive. The magnitude of responses for the used smallest concentrations was about 0.5...1.5%, and the response time was no longer than tens of seconds. All the mentioned types of sensitive films were used in the sensor array for identification of explosive substances. For this test, a saturated pair of analytes (MNB, 2-MNT) was used, at the concentration of about 200 ppm.

In what followed, six consecutive series of measurements aimed at responses to explosive simulants were carried out. Some of the typical obtained relative responses are shown in Figs 7 and 8. Note that the used films were unstable under the influence of these analytes. In particular, after the end of the analyte exposure, a significant drift of the base line of the sensors conductivity was observed, especially noticeable with nitrobenzene and 2-nitrotoluene. Also, during each subsequent series of measurements, a clear trend of the increasing response to nitrobenzene was observed for the CNT/P3MT-Cl film, and the decrease of response to 2-nitrotoluene for the TiO₂/PANI-DBSA film, respectively.

For the discriminant analysis, the responses of all sensors were combined into three variants of a 2-element and one variant of 3-element sensor sets, and projected onto the corresponding principal components plane.

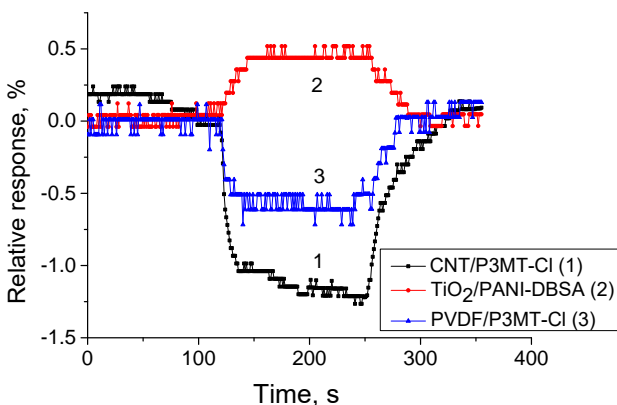


Fig. 7. Typical responses of the sensors based on CNT/P3MT-Cl, TiO₂/PANI-DBSA, and PVDF/P3MT-Cl sensitive films to the exposure in 2-MNT vapor at the concentration of 200 ppm. (Color online.)

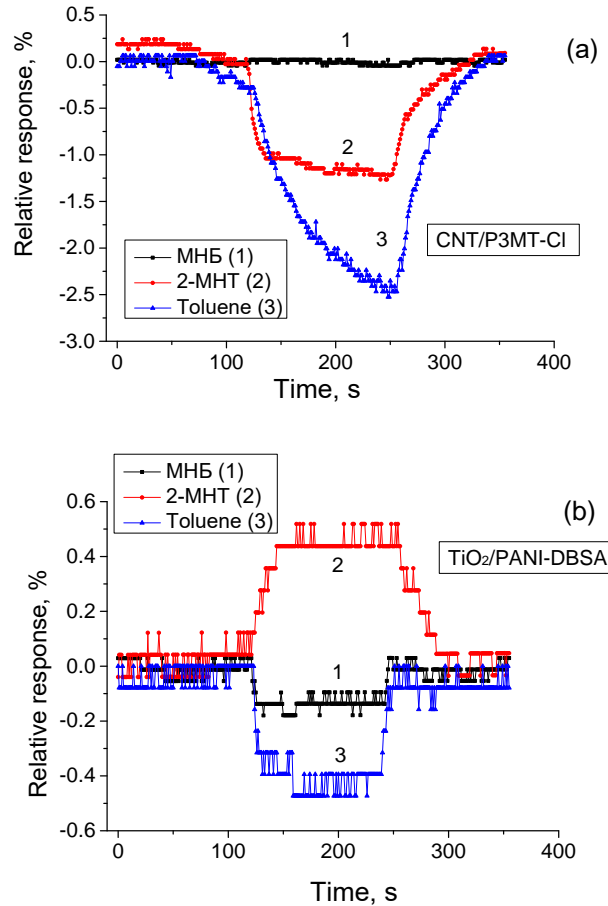


Fig. 8. Typical responses of the sensors based on CNT/P3MT-Cl (a) and TiO₂/PANI-DBSA (b) sensitive films to the injection of 2-MNT, MNB vapors at the concentration of 200 ppm; for comparison, responses to the same concentration of toluene are also added. (Color online.)

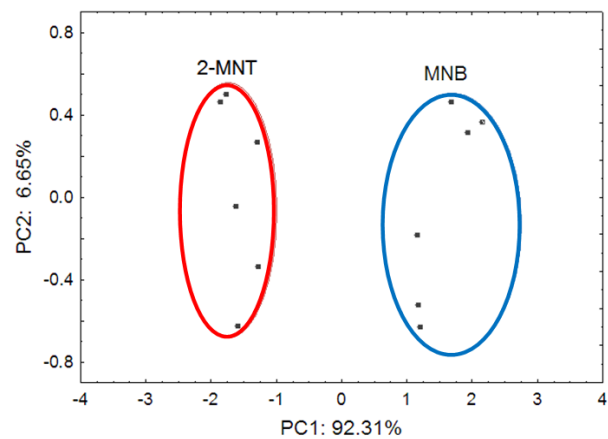


Fig. 9. Projections of sensor responses onto the plane of principal components for a 3-element sensor array based on sensitive layers of CNT/P3MT-Cl, PVDF/P3MT-Cl, TiO₂/PANI-DBSA nanocomposites with respect to two explosives simulants (MNB and 2-MNT); the encircled areas indicate the scattering of experimentally obtained responses to saturated vapors of the corresponding substances.

Fig. 9 shows these projections of the responses to the explosive simulants for the most successful combination of sensors, consisting of all three of the used sensors (with the three different types of chemiresistive films). It can be seen that well-separated areas corresponding to the specified classes of substances at the concentrations close to saturated vapors are formed on the plane.

At the same time, it is shown that a set of only two sensors based on the sensitive layers of CNT/P3MT-Cl and TiO₂/PANI-DBSA also provides a successful identification of the explosive substance simulants. Despite the fact that the used chemiresistive films turned out to be unstable in presence of the vapors of involved analytes, the confident identification of simulants with the tested variants of “electronic nose” was possible.

4. Conclusion

Conclusions regarding to the QCM sensors with calixarene sensitive layers

Sensitivity and selectivity to a number of imitators of explosive substances by using the quartz crystal microbalance has been carried out. When interacting with explosive substance simulants, CAs with amino groups in the upper rim and paraffins of various structures in the lower rim were the most sensitive. Alkaline properties of amino groups can provide electrovalent and ionic types of bonds with acid groups of nitro compounds. CAs with tert-butyl groups in the upper rim turned out to be less sensitive.

Research by the QCM method was carried out in the actual concentration range from 1 to 100 ppm by appropriate dilution of saturated analyte vapors. The detection limit, depending on the type of analyzed explosive substance, ranged from 1 to 10 ppm, which corresponds to the MPC in the operation zones for these compounds. The response rate was at the level of 10 s. It has been shown that among the tested set of derived calix[4]arene films there are samples with a fairly high selective sensitivity, which can be successfully used as sensitive layers in chemosensory systems.

Conclusions regarding the chemiresistive sensors with the nanocomposite ECP layers

As a result of the performed researches, three types of chemiresistive sensors suitable for detection of selected explosive substance simulants were determined. It has been shown that an array of the sensors of these types, due to variations in selectivity to different analytes, is able to reliably identify explosives as classes regardless of their concentrations in accordance with the “electronic nose” principle. It has been ascertained that in the context of development of a portable device for detecting explosives, it is advisable to use the two composite films of the CNT/P3MT-Cl and TiO₂/PANI-DBSA types, as the most sensitive with respect to the tested simulant substances.

The advantages of chemiresistive sensors include their fairly low response time, small size, and ease of measurement, which enable to create a portable device with autonomous power supply. The disadvantages of these sensors include their low selectivity, which requires a certain amount of time for the subsequent numerical processing of the signals recorded from an array of sensors forming an “electronic nose”, as well as the need for initial adaptation and “training” the sensors by using their exposition in vapors of the substances subjected to analysis in order to stabilize the sensor response baseline.

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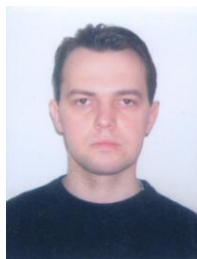
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Детектування імітаторів вибухонебезпечних нітроароматичних сполук хемосенсорними системами на основі п'єзокварцових та резистивних масивів сенсорів

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Анотація. Роботу присвячено дослідженню можливості швидкого детектування та наступної ідентифікації вибухонебезпечних речовин (ВНР) за допомогою масивів сенсорних елементів двох типів: п'єзокварцових кристалічних мікровагів та хеморезистивних електродів. Як чутливі шари для сенсорів були використані тонкі шари відповідно похідних каліксаренових сполук та композитів електропровідних полімерів. Як імітатори ВНР було вибрано кілька типів нітроароматичних речовин із ряду нітротолуолів: О-Нітротолуол (2-МНТ) та Нітробензол (МНБ), концентрація цих летких сполук варіювалася у межах від 10 до 100 ppm. Поріг детектування в залежності від типу аналізованих ВНР становив від 1 до 10 ppm для п'єзокварцових сенсорів з каліксареновими чутливими плівками, швидкодія відгуків була в межах 10...20 с для п'єзокварцових сенсорів та до 1 хв – для хеморезистивних сенсорів. Показано, що серед випробуваного набору каліксаренів є зразки з високою селективною чутливістю. Продемонстровано можливість якісної ідентифікації вибухонебезпечних речовин у діапазоні досить малих концентрацій з використанням статистичних методів розпізнавання хімічних образів (т.з. “електронного носу”).

Ключові слова: кварцовий кристалічний резонатор, каліксареновий рецептор, хеморезистивний електрод, електропровідний полімер, сенсорний масив, вибухонебезпечна речовина.